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Low energy mechanical treatment of non-stoichiometric titanium carbide powder

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ABSTRACT

Introduction. The practical significance of non-stoichiometric titanium carbides TiC$_x$ in various fields of technology and in medicine is expanding. In this regard, it is important to investigate both methods of obtaining titanium carbide powder and its properties in a wide range of stoichiometry. One of the effective ways to influence the physical and mechanical properties of powder systems is its mechanical treatment. Under shock-shear action, which is realized during processing in a ball mill, mechanical energy is transferred to the powder system, as a result of which it is ground, centers with increased activity on newly formed surfaces are formed; phase transformations, crystal lattice deformation, amorphization, formation of defects, etc. are possible. **The aim of this work** is to study the effect of low-energy mechanical treatment in a ball mill on the structure, phase composition and parameters of the fine crystal structure of non-stoichiometric titanium carbide powder obtained by reduction of titanium oxide with carbon and calcium. **Materials and methods.** Powder of titanium carbide TiC, obtained by calcium carbonization of titanium oxide was investigated. The powder was treated in a drum type ball mill. The structure of the powders before and after treatment was studied using the Philips SEM 515 scanning electron microscope. The specific surface area was determined by the BET method. The phase composition and parameters of the fine crystal structure of powder materials were investigated by X-ray analyzes. **Results and discussion.** It was established that an increase of the time of mechanical treatment in a ball mill of a non-stoichiometric titanium carbide powder TiC$_{0.7}$ leads to an increase in the specific surface area of the powder from 0.6 to 3.4 m^2 / g, and the average particle size calculated from it decreases from 2 μm to 360 nm. It is shown that in the process of treatment of the non-stoichiometric titanium carbide TiC$_{0.7}$ powder, its structural phase state changes. Powder particles consist of two structural components with different atomic ratio of carbon to titanium: TiC$_{0.65}$ and TiC$_{0.48}$. Mechanical treatment of titanium carbide powder leads to a decrease in the microstresses of the TiC$_x$ crystal lattice and the size of coherently diffracting domains (CDD) from 55 to 30 nm for the TiC$_{0.48}$ phase. For the TiC$_{0.65}$ phase, with an increase in the duration of mechanical treatment, as well as for TiC$_{0.48}$, the size of CDD decreases, and the level of microdistortions of the crystal lattice increases. This indicates that in the process of mechanical treatment, not only the grinding of powder particles occurs, but also an increase in its defects.

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Introduction

Materials based on titanium carbide are of great practical and scientific interest today, which is mainly due to a unique combination of its properties. Titanium carbide that possesses such properties as high wear resistance and low friction coefficient, high resistance to aggressive media, high hardness, and resistance to thermomechanical loads, is in demand in various fields for production of protective and wear-resistant coatings, heat-resistant ceramics, cutting tools [1–6], and biomaterials in medicine [7, 8]. Porous titanium carbide is a unique adsorbent to clean the environment from pollutants [9]. In addition, titanium carbide powder is also used as a promising material for hydrogen storage [10]. To date, methods of obtaining powders and the study of various properties of titanium carbide have been addressed in numerous studies [11–22]. The main properties are largely studied for stoichiometric or close-to-stoichiometric titanium carbides TiC_x. A fundamental distinguishing feature of titanium carbide TiC_x is its wide homogeneity region in the carbon concentration range $x = 0.33…1.0$, i.e. the crystal structure is retained even at carbon vacancy concentration of up to 67 %. Depending on the composition, synthesis conditions, and heat treatment, TiC_x carbide can be in a disordered or an ordered state [23]. The properties of TiC in this range of vacancy concentrations can change significantly [23–26], which makes it possible to obtain materials with the required performance characteristics. Practical significance of non-stoichiometric titanium carbides TiC_x in engineering, industry, and in medicine is expanding; therefore, it is important to study methods of obtaining non-stoichiometric titanium carbide TiC_x and to investigate its properties in a wide range of vacancy concentration. Mechanical treatment [27–34], in particular, treatment in a ball mill [34], is one of the most effective ways to influence physical and mechanical properties of powder systems. The energy received by the powder during mechanical treatment, and, accordingly, the activation effects depend on the type of the transmitted action. Mechanical treatment causes such effects as shock, abrasion and crushing, or its combination [25, 27–32, 34]. Ball mill treatment induces a shock-shear effect, when mechanical energy is transferred to the powder system, which results in both grinding of powder particles with the formation of new surfaces and centers of increased activity on these surfaces, and crystal lattice deformation. The process can also involve phase transformations, partial amorphization, formation of various types of defects, etc. However, virtually no systematic studies have been conducted to control, within certain limits, the dispersion, microstructure, stoichiometry of the products after treatment.

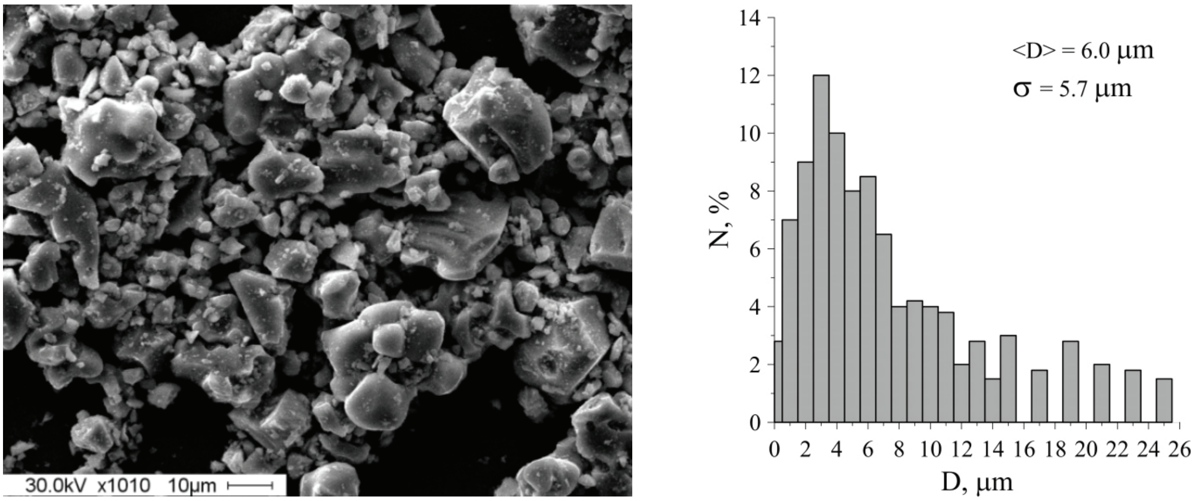
The purpose of this work is to investigate the effect of low-energy mechanical treatment in a ball mill on the structure, phase composition, and parameters of the fine crystal structure of non-stoichiometric titanium carbide powder obtained by reduction of titanium oxide with carbon and calcium.

Materials and research methods

TiC powder of composition: Ti – 15 vol. % C obtained by calcium carbide reduction of titanium oxide was the study object. TiC powder was subjected to dry mechanical treatment (MT) in a ball mill with corundum grinding bodies. The mill rotational speed was 40 rpm. The treatment time varied from 5 to 100 hours. The powder structure was studied before and after MT using a Philips SEM 515 scanning electron microscope. The specific surface area (SSA) was determined with a SORBI 4.1 device (META, Novosibirsk) by 4-point BET method using low-temperature nitrogen adsorption. The bulk density of the initial powder was determined by the funnel method according to the international standard ISO 3923-1: 2018. The phase composition and parameters of the fine crystal structure of powder materials were investigated by X-ray phase and X-ray structural analyses using a DRON-type X-ray diffractometer (Russia) with filtered CuKα radiation in a 2θ scanning mode from 30 to 145 degrees. The exposure at each point provided a statistical accuracy of not less than 0.5%. The diffraction profiles were approximated by the Lorentz function. The size of the coherent diffraction domains (CDD) was calculated using the Scherrer equation [35] from the first line of X-ray profiles (111), and the microdistortion of the crystal lattice was calculated using the Stokes-Wilson formula [36] from the last distinguishable line of X-ray profiles (511).

Results and discussion

Figure 1, *a* shows a SEM image of the initial TiC powder. The initial TiC powder is weakly agglomerated and consists mainly of irregular shaped particles. Along with the fragmented and spongy particles characteristic of powders obtained by the reduction method, the powder contains particles with a shape close to spherical. Powders show a wide unimodal particle size distribution; along with small (up to 2 μm) particles, the powder contains large, agglomerated particles up to 25 μm in size (Figure 1, *b*).



a *b*

Fig. 1. SEM image (*a*) and particle size distribution (*b*) of the initial TiC powder

The average particle size, including agglomerates, calculated by the method reported in [37] is 6 μm, and the average crystallite size determined from the X-ray reflection broadening is 55 nm. The SSA of the initial powder was 0.6 m^2/g, and the bulk density was $0.1\rho_{theor}$.

The SSA of the titanium carbide powder versus the MT time is shown in Figure 2. It can be seen that the SSA of the initial powder was low, and low-energy treatment caused its noticeable changes. With an increase in the mechanical treatment, the SSA significantly increased.

The most intensive increase in the SSA (more than 5 fold), occurred during MT within up to 50 hours, and with further increase in the MT time up to 100 hours, the dependence saturated and the SSA was 3.4 m^2/g. The calculation of the powder particle size from the SSA values under assumption of particle sphericity showed that its size decreases from 2 μm to 360 nm at increased MT time (Figure 2). The particle size of the TiC_x powder during treatment can be influenced by both grinding parameters and changes in its stoichiometry. In particular, in [25, 32, 34], it is shown that an increase in the time of grinding of TiC_x powder leads to a decrease in the particle size, and under similar grinding conditions, the size of the particles of the crushed powder depends on the relative content of nonmetals x, i.e. on the stoichiometry of TiC_x carbide [23]. The change in the titanium carbide stoichiometry during MT can be seen based on the analysis of the X-ray diffraction patterns before and

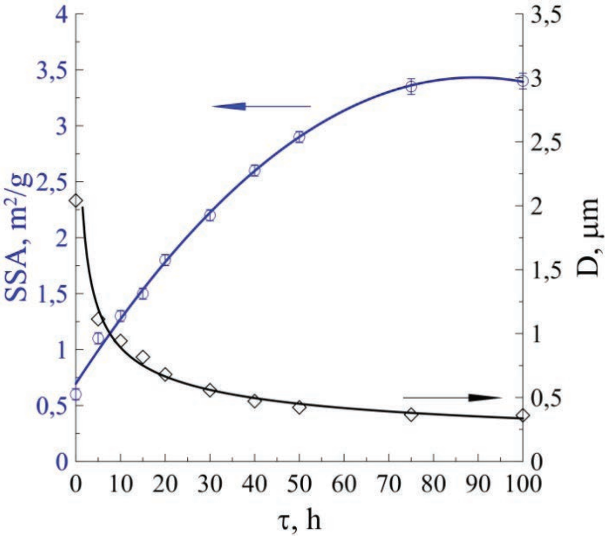


Fig. 2. Change in the specific surface area (SSA) and the TiC powder particle size calculated from these values vs. the mechanical treatment time

after treatment. Figure 3 shows the X-ray diffraction patterns of the initial powder and that mechanically treated for different time. The diffraction peaks in all X-ray diffraction patterns correspond to the cubic TiC_x lattice of the NaCl type. No peaks that belong to other phases or milling products from corundum grinding bodies were found in the X-ray diffraction patterns. The crystal lattice parameter of the powder in the initial state corresponds to the composition $TiC_{0.7}$. An increase in the time of MT of TiC_x powder does not lead to a change in the phase composition. However, a detailed analysis of the X-ray diffraction patterns showed that during MT of the powders their diffraction patterns change, the diffraction reflections are divided into two components.

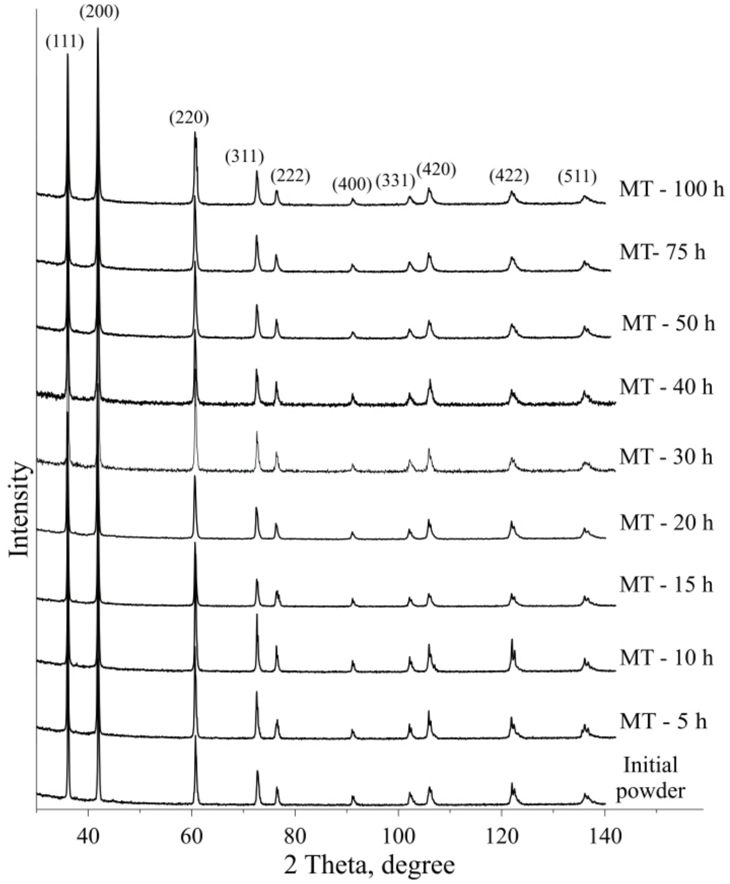
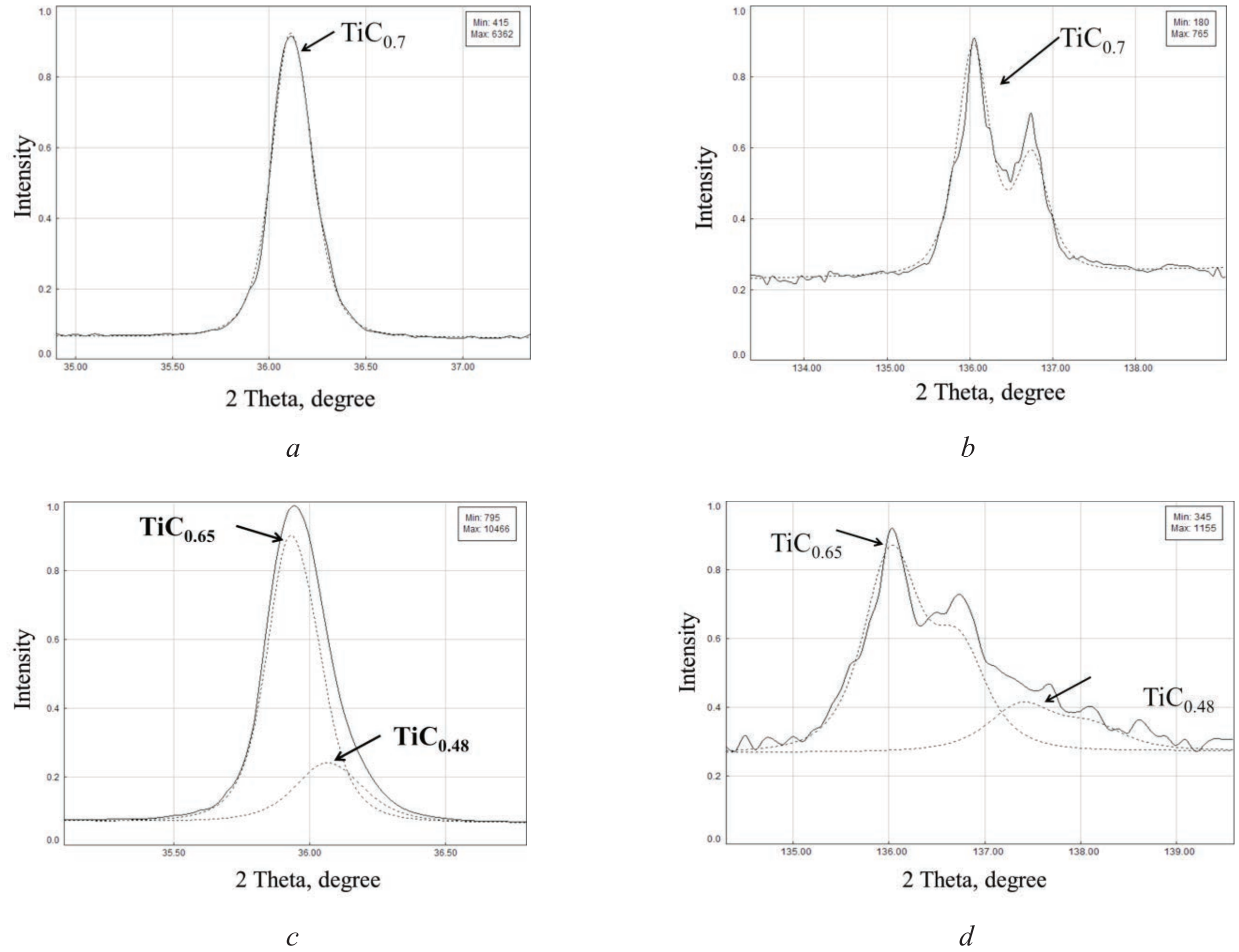


Fig. 3. X-ray diffraction patterns of TiC_x powder vs. mechanical treatment time

Figure 4 shows fragments of the diffraction patterns of the (111) and (511) planes of the powder in the initial state and that after mechanical treatment.

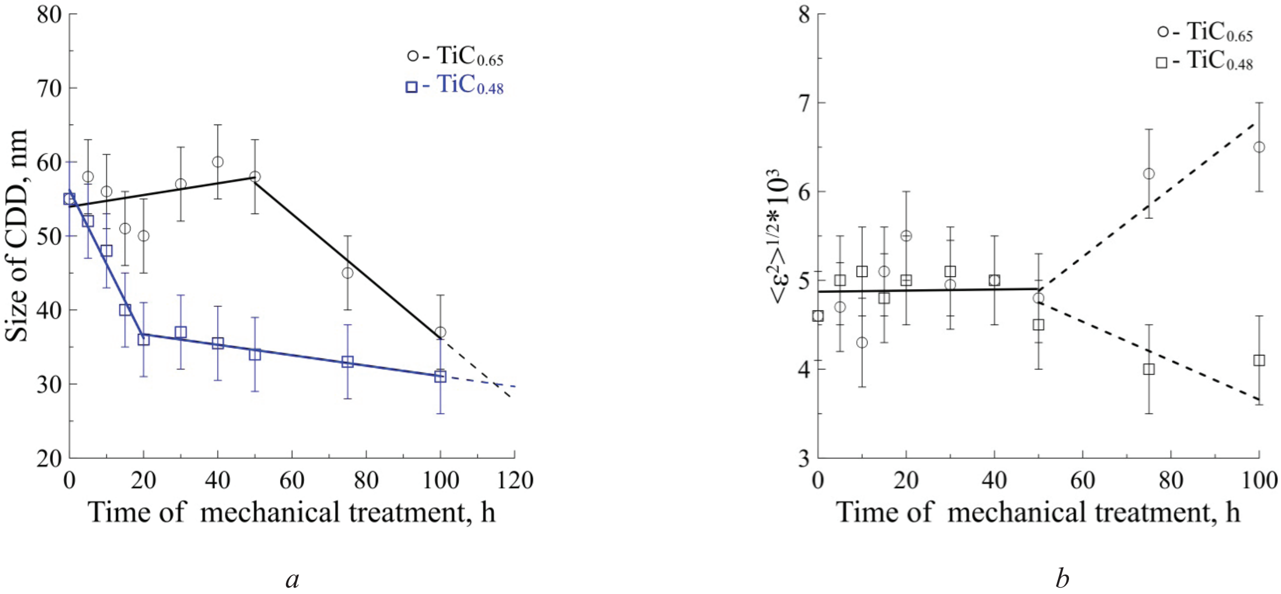
All diffraction profiles of the powder in the initial state are described by one function with high statistical accuracy (Figure 4, *a*, *b*). The diffraction profiles of the powders after MT are divided into two components (Figure 4, *c*, *d*). This may indicate a different content of carbon (x) in TiC_x powders [32-34, 38-40] accompanied by occurrence of point defects, such as structural vacancies, or it can be related to ordering and disordering processes. The effect of structural defects on properties of the non-stoichiometric compounds is very significant [38]. In [38-40], it is assumed that a wide range of homogeneity from $TiC_{0.48}$ to $TiC_{1.00}$ is exhibited by exclusively disordered TiC_x and, under specific conditions, ordered phases of M_2C, M_3C_2, and M_6C_5 type with cubic, triclinic, or rhombic lattices can form in it. In our case, the diffraction reflections correspond to the compositions $TiC_{0.65}$ and $TiC_{0.48}$. An increase in the MT time for the TiC_x powder from 5 to 100 hours does not lead to a change in the atomic ratio of carbon to titanium in both phases. Figure 5 shows the dependences of the CDD size (*a*) and crystal lattice microdistortions (*b*) on the MT time for structural components of the powders $TiC_{0.65}$ and $TiC_{0.48}$. Figure 5, *a* shows that with an increase in the MT time to



a *b*

c *d*

Fig. 4. Fragments of the X-ray diffraction patterns of planes (111) (*a*, *c*) and (511) (*b*, *d*) of the powder in the initial state (*a*, *b*) and that after mechanical treatment (*c*, *d*)



a *b*

Fig. 5. CDD size (a) and crystal lattice microdistortions (b) vs. mechanical treatment time for two structural states TiC$_{0.65}$ and TiC$_{0.48}$

50 hours, the CDD size for $TiC_{0.65}$ almost does not change, and then with a further increase in the MT time to 100 hours, it decreases. With an increase in the MT time to 20 hours for $TiC_{0.48}$, a sharp decrease in the CDD size from 55 nm to 35 nm is first observed, and with a further increase in the MT time to 100 hours, the CDD size decreases insignificantly.

With an increase in the MT time, the values of the CDD sizes for the structural components of the powders $TiC_{0.65}$ and $TiC_{0.48}$ approach each other, and the extrapolation of the dependences of the CDD sizes shows that after treatment for 115 hours, the CDD sizes for $TiC_{0.65}$ and $TiC_{0.48}$ will become equal and make about 30 nm. A different behavior of the curves is observed for the dependences of the crystal lattice microdistortions on the MT time for the structural components of the powders $TiC_{0.65}$ and $TiC_{0.48}$ (Figure 5, *b*). It can be seen that within up to 50 hours of exposure, the microdistortions of the crystal lattice of $TiC_{0.65}$ and $TiC_{0.48}$ are close in values and virtually do not depend on treatment time. A further increase in the MT time to 100 hours increases microdistortions of the $TiC_{0.65}$ crystal lattice and decreases microdistortions of the $TiC_{0.48}$ crystal lattice. The difference in the dependences of the CDD size and crystal lattice microdistortions on the MT time for the $TiC_{0.48}$ and $TiC_{0.65}$ phases can be due to a significant effect of the crystal lattice defects: within long treatment time, relaxation of the $TiC_{0.48}$ crystal lattice microdistortions can be caused by vacancy ordering phenomena, which occur in more non-stoichiometric TiC_x, followed by formation of various superstructures [38, 40]. For an accurate description of the processes occurring in such carbides during mechanical treatment, it is necessary to conduct neutron diffraction studies.

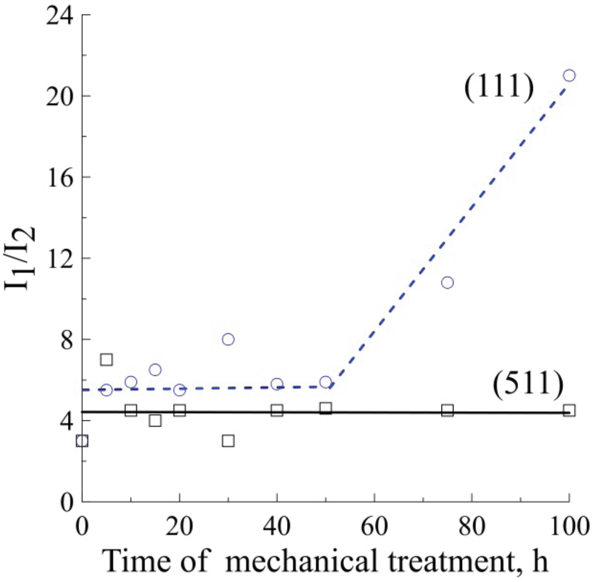


Fig. 6. Ratio of the peak intensities for $TiC_{0.65}$ and $TiC_{0.48}$ depending on the mechanical treatment time for peaks (111) and (511)

The dependences of the ratio of the peak intensities calculated for reflections (111) and (511) of the structural components of the powders $TiC_{0.65}$ and $TiC_{0.48}$ on the MT time are shown in Figure 6.

It can be seen that the ratio of the peak intensities for the (111) reflection does not change up to 50 hours of MT, and then the effect of the impact of MT can be observed; the peak intensity ratio for the (111) reflection increases sharply with an increase in the MT time up to 100 hours. The calculation of the peak intensity ratio for the (511) reflection showed that an increase in the MT time does not cause a change in the peak ratio. The results obtained are in good agreement with the results reported in [25, 32], where similar dependences of the changes in the CDD size and crystal lattice microdistortions were obtained during high-energy treatment. Long time treatment led not only to powder grinding, but also to a strong distortion of the crystal lattice and an increase in the number of defects. Mechanical treatment causes not only the dispersion of particles of titanium carbide powder, but also its activation due to the accumulation of microdamages.

Conclusions

It was found that with an increase in the time of mechanical treatment of non-stoichiometric titanium carbide powder TiC in a ball mill, the specific surface area of the powder increases from 0.6 to 3.4 m^2/g, and the average particle size calculated from it decreases from 2 to 0.36 μm.

It is shown that the composition of the powder in the initial state corresponds to $TiC_{0.7}$, and after mechanical treatment, particles of nonstoichiometric titanium carbide consist of two structural components with different atomic ratio of carbon to titanium: $TiC_{0.65}$ and $TiC_{0.48}$.

Mechanical treatment of the titanium carbide powder leads to a decrease in the microstresses of the TiC_x crystal lattice and in the CDD size from 55 to 30 nm for the $TiC_{0.48}$ phase. For the $TiC_{0.65}$ phase, with an increase in mechanical treatment time, the CDD size decreases similar to that for $TiC_{0.48}$, and the level of microdistortions of the crystal lattice increases. This indicates that mechanical treatment results in not only grinding of powder particles, but it also increases its defectiveness.

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Conflicts of Interest

The authors declare no conflict of interest.